

DE 19,62,951 A 1

---

Job No.: 1505-87819

Translated from German by the Ralph McElroy Translation Company  
910 West Avenue, Austin, Texas 78701 USA

FEDERAL REPUBLIC OF GERMANY  
GERMAN PATENT OFFICE  
PATENT NO. DE 196 29 951 A 1  
(Offenlegungsschrift)

Int. Cl.<sup>6</sup>: A 61 K 7/06  
Filing No.: 196 29 951.9  
Filing Date: July 25, 1996  
Publication Date: January 29, 1998

HAIR CARE PREPARATION IN THE FORM OF A TRANSPARENT OR TRANSLUCENT  
MICROEMULSION OF OIL-IN-WATER TYPE

Inventors: Dr. Jorg Schreiber  
22087 Hamburg, DE

Michael Demitz  
22529 Hamburg, DE

Dr. Jan-Henric Riedel  
22307 Hamburg, DE

Applicant: Beiersdorf AG  
20253 Hamburg, DE

Addition to: 195 09 079.9

References cited: DE 30 01 300 A1  
FR 15 20 909  
US 44 12 035  
EP 03 81 318 A2  
EP 03 49 150 A2  
EP 02 70 249 A2  
EP 00 58 853 A2  
Chemical Abstract, Vol. 117, 1992,  
91069c

The following information was taken from document submitted by the applicant.

[Abstract]

Hair care preparations in the form of a transparent or translucent microemulsion of oil-in-water type,

- consisting of an oil phase selected from among the silicone oils, and an aqueous phase
- containing:
  - one or more polyethoxylated O/W emulsifiers,
- optionally also containing one or more W/O emulsifiers,
- also containing at least one cationic surfactant selected from among surfactants that do not have film-forming properties,
- an emulsifier content less than 2.0 wt% with respect to the total weight of the emulsion.

This invention concerns cosmetic hair care preparations.

This invention concerns cosmetic active agent combinations and preparations containing such combinations for use on hair. In particular, this invention concerns cosmetic active agent combinations and preparations for care of the hair and scalp. In a preferred embodiment this invention concerns active agent combinations and preparations that serve to strengthen the individual hairs and/or to give the hairstyle, as a whole, hold and fullness.

Roughly generalizing, human hair can be divided into the living part, the hair root, and the dead part, the hair shaft. In turn, the hair shaft consists of the medulla, which however has become unimportant for modern man due to developmental history and has regressed and is often entirely lacking in the case of thin hair, then the cortex that surrounds the medulla, and the cuticle that surround the totality of medulla and cortex.

In particular, the cuticle, and also the keratinous region between the cuticle and cortex, are exposed to particular stress due to environmental effects, combing and brushing, and also due to hair treatment, especially hair dyeing and hair shaping, permanent wave processes, for example.

When there is particularly aggressive stress, for example bleaching with oxidants like hydrogen peroxide, in which the pigments distributed in the cortex are destroyed by oxidation, the inner part of the hair can also be affected. If human hair is to be permanently dyed, oxidizing hair dying processes are the only possibilities in practice. In the case of oxidative hair dyeing the formation of dye chromophores takes place through the reaction of precursors (phenols, aminophenols, less often diamines) and bases (mostly p-phenylenediamine) with the oxidation agent, mostly hydrogen peroxide. Hydrogen peroxide concentrations in this case are usually around 6%.

Usually one starts from the fact that besides the coloring effect a bleaching effect also takes place through the hydrogen peroxide. In oxidatively dyed human hair microscopic holes

can be detected at the sites at which melanin granules were present, similar to the case with bleached hair. The fact is that the oxidation agent hydrogen peroxide reacts not only with the dye precursors, but also with the substance of the hair and in doing so can possibly cause damage to the hair.

Also, shampooing with aggressive surfactants can stress the hair, or at least can reduce its appearance or the appearance of the hairstyle. For example, certain water-soluble hair components (for example urea, xanthin, keratin, glycogen, citric acid, lactic acid) can be leached out by shampooing.

For these reasons hair care cosmetics that are intended to be rinsed out after acting on the hair and in some cases which are supposed to remain on the hair have long been used. The latter cosmetics are formulated so that they serve not only to provide care to the individual hairs, but also to give the hairstyle a better appearance overall, for example by conferring greater fullness to the hair, fixing the hairstyle over a long period of time or improving its styleability.

The property of fullness is ascribed to a hairstyle, for example, when the hair does not lie flat on the scalp on the treatment and is readily styleable.

The property of volume is ascribed to a hairstyle, for example, when the hair after treatment has fullness and springiness. The property of body is ascribed to a hairstyle, for example, when the hair volume remains large even under external disturbing influences.

For example, the combability of the hair can be considerably improved by quaternary ammonium compounds. Such compounds are absorbed on the hair and frequently can still be detected on the hair after several shampooings.

However, the prior art lacks active agents and preparations that are able to provide care to damaged hair in a satisfactory way. In addition, preparations that are intended to give the hairstyle fullness have often proved to be unsuitable, at least they were unsuitable to be used as hair care preparations. Preparations of the prior art that are used to fix the hairstyle as a rule contain, for example, viscous components, which run the danger of producing a sticky feel, which frequently must be compensated by a clever formulation.

For this reason the task was to create remedies for the disadvantages of the prior art.

Common presentation forms of cosmetic or dermatologic preparations are finely divided multiphase systems in which one or more fat or oil phases is present in addition to one or more aqueous phases. Of these systems the true emulsions are again the most common.

In simple emulsions finely divided droplets of one phase (water droplets in W/O or lipid droplets in O/W emulsions) surrounded by an envelope of emulsifier are present in the second phase. The droplet diameter of the usual emulsions lies in the range from about 1  $\mu\text{m}$  to about 50  $\mu\text{m}$ . Such "macroemulsions" are, without the addition of other coloring additives, milky white and opaque. Finer "macroemulsions," whose droplet diameters lie in the range from about  $10^{-1}$

$\mu\text{m}$  to about  $1\ \mu\text{m}$ , are, again without the coloring additives, bluish white in color and not transparent.

Only micellar and molecular solutions with particle diameters smaller than about  $10^{-2}\ \mu\text{m}$  appear clear and transparent.

The droplet diameter of transparent or translucent microemulsions, in contrast, lies in the range of about  $10^{-2}\ \mu\text{m}$  to about  $10^{-1}\ \mu\text{m}$ . Such microemulsions for the most part have a low viscosity. The viscosity of many microemulsions of O/W type is comparable to that of water.

An advantage of microemulsions is that active agents can be present in the disperse phase in a more finely dispersed form than in the disperse phase of "macroemulsions." Another advantage is that because of their low viscosity they can be sprayed. If microemulsions are used as cosmetics, the corresponding products are in general characterized by high cosmetic elegance.

It is disadvantageous with the microemulsions of the prior art that a high content of one or more emulsifiers always has to be used, since the small droplet size produces a large interface between the phases, which as a rule has to be stabilized by emulsifiers.

Basically speaking, the use of the usual cosmetic emulsifiers is safe. Nevertheless, emulsifiers, like any chemical substance in the end, can give rise to allergic or hypersensitive reactions in individual cases.

For instance, it is known that certain photodermatoses can be triggered by emulsifiers as well as by various fats and simultaneous exposure to sunlight.

A particular task of this invention was to make available finely divided preparations of the oil-in-water type with an emulsifier content that is as low as possible, which do not have the disadvantages of the prior art and which can be used for the most varied cosmetic and/or dermatologic applications, for example those described above. Another task of the invention was to add to the limited number of finely divided preparations of the oil-in-water type in the prior art.

It is substantially known that hydrophilic emulsifiers, namely polyethoxylated and polypropoxylated emulsifiers, change their solubility behavior from water-soluble to fat-soluble with increasing temperature. A characteristic of the hydrophilicity of given emulsifier is its HLB value.

The HLB value for polyol fatty acid ester is given by the relationship

$$\text{HLB} = 20 \cdot (1 - S/A) \quad (\text{Formula I})$$

For a group of emulsifiers whose hydrophilic component consists only of ethylene oxide components, the following relationship is valid

$$\text{HLB} = E/5 \quad (\text{Formula II})$$

where S is the saponification number of the ester,

A is the acid number of the recovered acid

E is the weight fraction of ethylene oxide (%) in the total molecule.

Emulsifiers with HLB values of 6-8 are in general W/O emulsifiers, while ones with HLB values of 8-18 are in general O/W emulsifiers.

Reference: "Cosmetic – Development, Production and Use of Cosmetic Agents" [in German], W. Umbach (Editor), Georg Thieme Verlag, 1988.

The temperature range in which the emulsifiers change their solubility is called the phase inversion temperature region. In this document the abbreviation "PIT" will also be used for the phase inversion temperature range.

The change of this solubility behavior is, as is known, expressed in that if a mixture of water, oil and O/W emulsifiers that after stirring yields an O/W emulsion under the PIT is brought to a temperature above the PIT, typically about 70-90°C, it can pass through the state of a microemulsion as an intermediate step, in order to finally produce a W/O emulsion above the PIT. If this emulsion is cooled, an O/W emulsion is again obtained, but one that now has a droplet size up to 200 nm.

Microemulsions of the prior art produced in this way, however, have the disadvantage that the droplet size is still quite high, so that the emulsion at room temperature has an opaque white to bluish color.

In addition, it is disadvantageous that microemulsions produced in this way can indeed be practically transparent at high temperature, thus, for example in the PIT, but upon cooling back to room temperature they again become nontransparent.

Thus, it was also a matter of remedying these problems.

Surprisingly, all of these tasks are solved by hair care preparations in the form of a transparent or translucent microemulsion of oil-in-water type,

- consisting of an oil phase and aqueous phase

- containing:

- one or more polyethoxylated O/W emulsifiers and/or

- one or more polypropoxylated O/W emulsifiers and/or

- one or more polyethoxylated or polypropoxylated O/W emulsifiers,

- optionally also containing one or more W/O emulsifiers

- also containing at least one cationic surfactant selected from surfactants that do not have film-forming properties

- an emulsifier content less than 2.0 wt%, with respect to the total weight of the emulsion.

Preferably, the preparations in accordance with the invention can be obtained by bringing a mixture of the basic components, consisting of water phase, oil phase, one or more of the O/W emulsifiers in accordance with the invention, optionally one or more W/O emulsifiers, and

optionally other auxiliary agents, additives and/or active agents, to a temperature within or above the phase inversion temperature range, and then cooling them back to room temperature.

Preparations in accordance with the invention have a low viscosity, are sprayable, are excellently suitable as vehicles for the most varied active agents, especially lipid-soluble active agents and are additionally characterized by excellent compatibility with the skin, hair and mucous membranes.

A solubilized preparation that can include, for example, polyethylene glycol alkyl ethers, was indeed described in JP-A-Hei-06[1994]/262060 (according to the Patent Abstracts of Japan). The oil phase of the disclosed examples, however, concerns the highly volatile heptane, which in current usage can hardly be viewed as an oil component, and definitely not as a cosmetic or pharmaceutical oil component. The microemulsions made in accordance with this teaching, in spite of the claim, cannot be viewed as cosmetics or drugs.

In addition, microemulsions are disclosed in US-A-4,146,499 that do contain ethoxylated raw materials, in which, however, the oil phase is typically represented by such non-physiologic components as benzene, tetrachloromethane, dichloromethane and fluorochlorocarbons. This document of the prior art could not point the way to the present invention, either.

EP-B-490 053 describes hair cure agents in the form of a microemulsions, which are characterized by the fact that they contain between 5.5 and 30 wt% surfactants. This document of the prior art could not show the way to the present invention, either.

The polyethoxylated or polypropoxylated or polyethoxylated and polypropoxylated O/W emulsifiers or the polyethoxylated or polypropoxylated or polyethoxylated and polypropoxylated O/W emulsifiers selected from the following group can be advantageous:

- the fatty alcohol ethoxylates of the general formula  $R-O-(CH_2CH_2-O)_n-H$ , where R is a branched or unbranched alkyl, aryl or alkenyl residue and n is a number from 10 to 50
- the ethoxylated lanolin alcohols,
- the polyethylene glycol ethers of the general formula  $R-O-(CH_2CH_2-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues and n is a number from 10 to 80,
- the fatty acid ethoxylates of the general formula  $R-COO-(CH_2CH_2-O)_n-H$ , where R is a branched or unbranched alkyl or alkenyl residue and n is a number from 10 to 40,
- the etherified fatty acid ethoxylates of the  $R-COO-(CH_2CH_2-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues and n is a number from 10 to 80,
- the esterified fatty acid ethoxylates of the general formula  $R-COO-(CH_2CH_2-O)_n-C(O)-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues and n is a number from 10 to 80

- the polyethylene glycol glycerol fatty acid esters of saturated and/or unsaturated, branched and/or unbranched fatty acids with a degree of ethoxylation between 3 and 50,
- the ethoxylated sorbitan esters with a degree of ethoxylation of 3 to 100,
- the cholesterol ethoxylates with a degree of ethoxylation between 3 and 50,
- the ethoxylated triglycerides with a degree of ethoxylation between 3 and 150,
- the alkyl ether carboxylic acids of the general formula  $R-O(-CH_2CH_2-O)_n-CH_2-COOH$  or their cosmetically or pharmaceutically acceptable salts, where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 5 to 30,
- the polyoxyethylenesorbitol fatty acid esters based on branched or unbranched alkanolic or alkenolic acids with a degree of ethoxylation from 5 to 100, for example of sorbeth type,
- the alkyl ether sulfates or the acids underlying these sulfates having the general formula  $R-O(-CH_2CH_2-O)_n-SO_3-H$ , with cosmetically or pharmaceutically acceptable cations, where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 1 to 50,
- the fatty alcohol propoxylates of the general formula  $R-O(-CH_2-CH(CH_3)-O)_n-H$ , where R represents a branched or unbranched alkyl or alkenyl residue and n is a number from 10 to 80,
- the polypropylene glycol ethers of the general formula  $R-O(-CH_2-CH(CH_3)-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues and n is a number from 10 to 80
- the propoxylated lanolin alcohols,
- the etherified fatty acid propoxylates of the general formula  $R-COO(-CH_2-CH(CH_3)-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues and n is a number from 10 to 80,
- the esterified fatty acid propoxylates of the general formula  $R-COO(-CH_2-CH(CH_3)-O)_n-C(O)-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues and n is a number from 10 to 80,
- the fatty acid propoxylates of the general formula  $R-COO(-CH_2-CH(CH_3)-O)_n-H$ , where R represent a branched or unbranched alkyl or alkenyl residue and n is a number from 10 to 80,
- the polypropylene glycol glycerol fatty acid esters of saturated and/or unsaturated, branched and/or unbranched fatty acids with a degree of propoxylation between 3 and 80
- the propoxylated sorbitan esters with a degree of propoxylation from 3 to 100
- the cholesterol propoxylates with a degree of propoxylation from 3 to 100
- the propoxylated triglycerides with a degree of propoxylation from 3 to 100



- the alkyl ether carboxylic acids of the general formula  $R-O-(CH_2-CH(CH_3)-O)_n-CH_2-CO-OH$  or their cosmetically or pharmaceutically acceptable salts, where R represents a branched or unbranched alkyl or alkenyl residue and n is a number from 3 to 50,

- the alkyl ether sulfates or the acids underlying the sulfates of the general formula  $R-O-(CH_2-CH(CH_3)-O)_n-SO_3-H$  with cosmetically or pharmaceutically acceptable cations where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 1 to 50,

- the fatty alcohol ethoxylates/propoxylates of the general formula  $R-O-X_n-Y_m-H$ , where R represents a branched or unbranched alkyl or alkenyl residue, where X and Y are not the same and in each case represent either an oxyethylene group or an oxypropylene group, and n and m independently are numbers from 5 to 50,

- the polypropylene glycol ethers of the general formula  $R-O-X_n-Y_m-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues, where X and Y are not the same and in each case represent either an oxyethylene group or an oxypropylene group and n and m independently represent numbers from 5 to 100,

- the etherified fatty acid propoxylates of the general formula  $R-COO-X_n-Y_m-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues, where X and Y are not the same and in each case represent either an oxyethylene group or an oxypropylene group and n and m independently are numbers from 5 to 100,

- the fatty acid ethoxylates/propoxylates of the general formula  $R-COO-X_n-Y_m-H$ , where R represents a branched or unbranched alkyl or alkenyl residue, where X and Y are not the same and in each case represents either an oxyethylene group or an oxypropylene group and n and m independently are numbers from 5 to 50.

It is especially advantageous when the polyethoxylated or polypropoxylated or polyethoxylated and polypropoxylated O/W emulsifier or the polyethoxylated or polypropoxylated or polyethoxylated and polypropoxylated O/W emulsifiers are selected from among

- the fatty alcohol ethoxylates of the general formula  $R-O-(CH_2CH_2-O)_n-H$ , where R is a branched or unbranched alkyl, alkenyl residue with 5-30 atoms and n is a number from 10 to 25,

- the ethoxylated lanolin alcohols with HLB values of 11-16, really especially advantageously with HLB values of 14-16,

- the polyethylene glycol ethers of the general formula  $R-O-(CH_2CH_2-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues with 5-30 C atoms and n is a number from 10 to 40,

- the fatty acid ethoxylates of the general formula  $R-COO-(-CH_2CH_2-O)_n-H$ , where R is a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 10 to 30,
- the etherified fatty acid ethoxylates of the  $R-COO-(-CH_2CH_2-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues with 5-30 C atoms and n is a number from 10 to 50,
- the esterified fatty acid ethoxylates of the general formula  $R-COO-(-CH_2CH_2-O)_n-C(O)-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues with 5-30 C atoms and n is a number from 10 to 50
- the polyethylene glycol glycerol fatty acid esters of saturated and/or unsaturated, branched and/or unbranched fatty acids with 6 to 26 C atoms with a degree of ethoxylation between 3 and 40,
- the ethoxylated sorbitan esters with a degree of ethoxylation of 3 to 30,
- the cholesterol ethoxylates with HLB values of 11-16, really especially advantageously with HLB values of 14-16
- the ethoxylated triglycerides with HLB values of 11-16, really especially advantageously with HLB values of 14-16
- the alkyl ether carboxylic acids of the general formula  $R-O-(-CH_2CH_2-O)_n-CH_2-COOH$  or their cosmetically or pharmaceutically acceptable salts, where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 10 to 20,
- the polyoxyethylenesorbitol fatty acid esters based on branched or unbranched alkanoic or alkenoic acids with a degree of ethoxylation from 10 to 80, for example of sorbeth type,
- the alkyl ether sulfates or the acids underlying these sulfates having the general formula  $R-O-(-CH_2CH_2-O)_n-SO_3-H$ , with cosmetically or pharmaceutically acceptable cations, where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 3 to 30,
- the fatty alcohol propoxylates of the general formula  $R-O-(-CH_2-CH(CH_3)-O)_n-H$ , where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 10 to 30,
- the polypropylene glycol ethers of the general formula  $R-O-(-CH_2-CH(CH_3)-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues with 5-30 C atoms and n is a number from 10 to 40
- the propoxylated lanolin alcohols with HLB values of 11-16, really especially advantageously with HLB values of 14.5-15.5,

- the fatty acid propoxylates of the general formula  $R-COO-(-CH_2-CH(CH_3)-O)_n-H$ , where R represent a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 10 to 40,

- the etherified fatty acid propoxylates of the general formula  $R-COO-(-CH_2-CH(CH_3)-O)_n-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues with 5-30 C atoms and n is a number from 10 to 30,

- the esterified fatty acid propoxylates of the general formula  $R-COO-(-CH_2-CH(CH_3)-O)_n-C(O)-R'$ , where R and R' independently represent branched or unbranched alkyl or alkenyl residues with 5-30 C atoms and n is a number from 10 to 50,

- the polypropylene glycol glycerol fatty acid esters of saturated and/or unsaturated, branched and/or unbranched fatty acids with 6 to 26 C atoms with a degree of propoxylation between 3 and 50

- the propoxylated sorbitan esters with a degree of propoxylation from 3 to 80

- the cholesterol propoxylates with HLB values of 11-16, really especially advantageously with HLB values of 14.5-15.5

- the propoxylated triglycerides with HLB values of 11-16, really especially advantageously with HLB values of 14.5-15.5

- the alkyl ether carboxylic acids of the general formula  $R-O-(-CH_2-CH(CH_3)-O)_n-CH_2-CO-OH$  or their cosmetically or pharmaceutically acceptable salts, where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 10 to 30,

- the alkyl ether sulfates or the acids underlying the sulfates of the general formula  $R-O-(-CH_2-CH(CH_3)-O)_n-SO_3-H$  with cosmetically or pharmaceutically acceptable cations where R represents a branched or unbranched alkyl or alkenyl residue with 5-30 C atoms and n is a number from 1 to 30.

The polyethoxylated or polypropoxylated or polyethoxylated and polypropoxylated O/W emulsifiers that are used are especially advantageously selected in accordance with the invention from the group of substances with HLB vales of 11-6, really especially advantageously with HLB values of 14-16, provided the O/W emulsifiers have saturated residues R and R'. If the O/W emulsifiers have unsaturated residues R and/or R' or if they are isoalkyl derivatives, the preferred HLB value of such emulsifiers can also be lower or higher.

It is advantageous to select the fatty alcohol ethoxylates from the groups of ethoxylated stearyl alcohols, cetyl alcohols, cetylstearyl alcohols (cetearyl alcohols). Especially preferred are: polyethylene glycol (13) stearyl ether (steareth-13), polyethylene glycol (14) stearyl ether (steareth-14), polyethylene glycol (15) stearyl ether (steareth-15), polyethylene glycol (16) stearyl ether (steareth-16), polyethylene glycol (17) stearyl ether (steareth-17), polyethylene

glycol (18) stearyl ether (steareth-18), polyethylene glycol (19) stearyl ether (steareth-19), polyethylene glycol (20) stearyl ether (steareth-20),

polyethylene glycol (12) isostearyl ether (isosteareth-12), polyethylene glycol (13) isostearyl ether (isosteareth-13), polyethylene glycol (14) isostearyl ether (isosteareth-14), polyethylene glycol (15) isostearyl ether (isosteareth-15), polyethylene glycol (16) isostearyl ether (isosteareth-16), polyethylene glycol (17) isostearyl ether (isosteareth-17), polyethylene glycol (18) isostearyl ether (isosteareth-18), polyethylene glycol (19) isostearyl ether (isosteareth-19), polyethylene glycol (20) isostearyl ether (isosteareth-20),

polyethylene glycol (13) cetyl ether (ceteth-13), polyethylene glycol (14) cetyl ether (ceteth-14), polyethylene glycol (15) cetyl ether (ceteth-15), polyethylene glycol (16) cetyl ether (ceteth-16), polyethylene glycol (17) cetyl ether (ceteth-17), polyethylene glycol (18) cetyl ether (ceteth-18), polyethylene glycol (19) cetyl ether (ceteth-19), polyethylene glycol (20) cetyl ether (ceteth-20),

polyethylene glycol (13) isocetyl ether (isoceteth-13), polyethylene glycol (14) isocetyl ether (isoceteth-14), polyethylene glycol (15) isocetyl ether (isoceteth-15), polyethylene glycol (16) isocetyl ether (isoceteth-16), polyethylene glycol (17) isocetyl ether (isoceteth-17), polyethylene glycol (18) isocetyl ether (isoceteth-18), polyethylene glycol (19) isocetyl ether (isoceteth-19), polyethylene glycol (20) isocetyl ether (isoceteth-20),

polyethylene glycol (12) oleyl ether (oleth-12), polyethylene glycol (13) oleyl ether (oleth-13), polyethylene glycol (14) oleyl ether (oleth-14), polyethylene glycol (15) oleyl ether (oleth-15),

polyethylene glycol (12) lauryl ether (laureth-12), polyethylene glycol (12) isolauryl ether (isolaureth-12),

polyethylene glycol (13) cetylstearyl ether (cetareth-13), polyethylene glycol (14) cetylstearyl ether (cetareth-14), polyethylene glycol (15) cetylstearyl ether (cetareth-15), polyethylene glycol (16) cetylstearyl ether (cetareth-16), polyethylene glycol (17) cetylstearyl ether (cetareth-17), polyethylene glycol (18) cetylstearyl ether (cetareth-18), polyethylene glycol (19) cetylstearyl ether (cetareth-19), polyethylene glycol (20) cetylstearyl ether (cetareth-20).

It is also advantageous to select the fatty acid ethoxylates from the following groups:

polyethylene glycol (20) stearate, polyethylene glycol (21) stearate, polyethylene glycol (22) stearate, polyethylene glycol (23) stearate, polyethylene glycol (24) stearate, polyethylene glycol (25) stearate, polyethylene glycol (12) isostearate, polyethylene glycol (13) isostearate, polyethylene glycol (14) isostearate, polyethylene glycol (15) isostearate, polyethylene glycol (16) isostearate, polyethylene glycol (17) isostearate, polyethylene glycol (18) isostearate, polyethylene glycol (19) isostearate, polyethylene glycol (20) isostearate, polyethylene glycol

(21) isostearate, polyethylene glycol (22) isostearate, polyethylene glycol (23) isostearate, polyethylene glycol (24) isostearate, polyethylene glycol (25) isostearate,

polyethylene glycol (12) oleate, polyethylene glycol (13) oleate, polyethylene glycol (14) oleate, polyethylene glycol (15) oleate, polyethylene glycol (16) oleate, polyethylene glycol (17) oleate, polyethylene glycol (18) oleate, polyethylene glycol (19) oleate, polyethylene glycol (20) oleate.

Sodium laureth-11 carboxylate can advantageously be used as ethoxylated alkyl ether carboxylic acid or its salt.

Sodium laureth-14 sulfate can advantageously be used as alkyl ether sulfate.

Polyethylene glycol (30) cholesteryl ether can be advantageously used as ethoxylated cholesterol derivative. Polyethylene (25) soy sterol has also proved to be suitable.

The polyethylene glycol (60) evening primrose glycerides can advantageously be used as ethoxylated triglycerides.

It is further advantageous to select the polyethylene glycol glycerol fatty acid esters from the group polyethylene glycol (20) glyceryl laurate, polyethylene glycol (22) glyceryl laurate, polyethylene glycol (22) glyceryl laurate, polyethylene glycol (23) glyceryl laurate, polyethylene glycol (6) glyceryl caprate/caprate, polyethylene glycol (20) glyceryl oleate, polyethylene glycol (20) glyceryl isostearate, polyethylene glycol (18) glycerol oleate/cocoate.

It is likewise good to select the sorbitan esters from the group polyethylene glycol (20) sorbitan monolaurate, polyethylene glycol (20) sorbitan monostearate, polyethylene glycol (20) sorbitan monoisostearate, polyethylene glycol (20) sorbitan monopalmitate, polyethylene glycol (20) sorbitan monooleate.

The following may be used as optional, but nevertheless advantageous in accordance with the invention, W/O emulsifiers: fatty alcohols with 8 to 30 carbon atoms, monoglycerol esters of saturated and/or unsaturated, branched and/or unbranched alkane carboxylic acids with a chain length of 8 to 24, especially 12-18 C atoms, diglycerol esters of saturated and/or unsaturated, branched and/or unbranched alkane carboxylic acids with a chain length of 8 to 24, especially 12-18 C atoms, monoglycerol ethers of saturated and/or unsaturated, branched and/or unbranched alcohols with a chain length of 8 to 24, especially 12-18 C atoms, diglycerol ethers of saturated or unsaturated, branched and/or unbranched alcohols with a chain length of 8 to 24, especially 12-18 C atoms, propylene glycol esters of saturated and/or unsaturated, branched and/or unbranched alkane carboxylic acids with a chain length of 8 to 24, especially 12-18 C atoms and sorbitan esters of saturated and/or unsaturated, branched and/or unbranched alkane carboxylic acids with a chain length of 8 to 24, especially 12-18 C atoms.

Especially advantageous W/O emulsifiers are: glyceryl monostearate, glyceryl monoisostearate, glyceryl monomyristate, glyceryl monooleate, diglycerol monostearate,

diglyceryl monoisostearate, propylene glycol monostearate, propylene glycol monoisostearate, propylene glycol monocaprylate, propylene glycol monolaurate, sorbitan monoisostearate, sorbitan monolaurate, sorbitan monocaprylate, sorbitan monoisooleate, sucrose distearate, cetyl alcohol, stearyl alcohol, arachidyl alcohol, behenyl alcohol, isobehenyl alcohol, selachyl alcohol, chimyl alcohol, polyethylene glycol (2) stearyl ether (steareth-2), glyceryl monolaurate, glyceryl monocaprate, glyceryl monocaprylate.

The oil phase of the microemulsions in accordance with the invention is advantageously chosen from the group of the esters of saturated and/or unsaturated, branched and/or unbranched alkane carboxylic acids with a chain length of 3 to 30 C atoms and saturated and/or unsaturated, branched and/or unbranched alcohols with a chain length of 3 to 30 C atoms, from the group of the esters of aromatic carboxylic acids and saturated and/or unsaturated, branched and/or branched alcohols with a chain length of 3 to 30 C atoms. Such ester oils can then advantageously be selected from the group consisting of isopropyl myristate, isopropyl palmitate, isopropyl stearate, isopropyl oleate, n-butyl stearate, n-hexyl laurate, n-decyl oleate, isooctyl stearate, isononyl stearate, isononyl isononanoate, 2-ethylhexyl palmitate, 2-ethylhexyl laurate, 2-hexyldecyl stearate, 2-octyldodecyl palmitate, oleyl oleate, oleyl erucate, erucyl oleate, erucyl erucate and synthetic, semi-synthetic and natural mixtures of such esters, for example jojoba oil.

In addition, the oil phase can be advantageously selected from the group of the branched and unbranched hydrocarbons and waxes, the silicone oils, dialkyl ethers, the group of the saturated and/or unsaturated, branched and/or branched alcohols, and the fatty acid triglycerides, namely the triglycerol esters of saturated and/or unsaturated, branched and/or branched alkane carboxylic acids with a chain length of 8 to 24, especially 12-18 c atoms. The fatty acid triglycerides can advantageously be selected from the group of the synthetic, semi-synthetic and natural oils, for example olive oil, sunflower seed oil, soy oil, peanut oil, rapeseed oil, almond oil, palm oil, coconut oil, palm kernel oil and the like.

Also, any mixtures of such oils and wax components can advantageously be used in the sense of this invention.

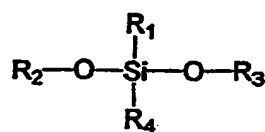
It can also optionally be advantageous to use waxes, for example cetyl palmitate, as the only lipid component of the oil phase. In such cases the O/W microemulsions in accordance with the invention can also optionally occur as microdispersions of solid wax particles.

Advantageously, the oil phase is selected from the group 2-ethylhexyl isostearate, octyldodecanol, isotridecyl isononanoate, isoeicosane, 2-ethylhexyl cocoate, C<sub>12-15</sub> alkyl benzoate, caprylic-capric acid triglyceride, dicaprylyl ether.

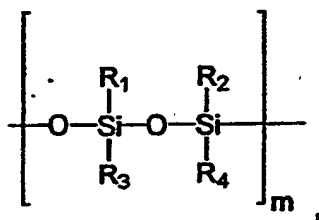
Especially advantageous are mixtures of C<sub>12-15</sub> alkyl benzoate and 2-ethylhexyl isostearate, mixtures of C<sub>12-15</sub> alkyl benzoate and isotridecyl isononanoate and mixtures of C<sub>12-15</sub> alkyl benzoate, 2-ethylhexyl isostearate and isotridecyl isononanoate.

Of the hydrocarbons paraffin oil, squalane and squalene can advantageously be used in the sense of this invention.

However, it is preferred to choose the oil phase of the preparations in accordance with the invention from the group of the cyclic and/or linear silicones. These can be in the form of a monomer, which as a rule is characterized by structural elements as follows:

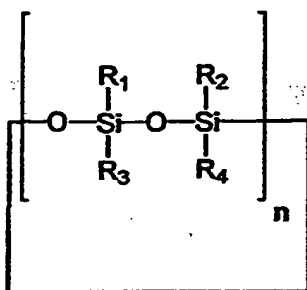


Linear silicones with several siloxy units that can be used advantageously in accordance with the invention are characterized in general by structural elements as follows:



where the silicon atom can be substituted with the same or different alkyl residue and/or aryl residues, which here are represented in a general way by the residues R<sub>1</sub>-R<sub>4</sub> (that is to say that the number of the different residues is not necessarily limited to 4). m can take on numbers from 2 to 200,000.

Cyclic silicones that can advantageously be used in accordance with the invention are in general characterized by structural elements as follows:



where the silicon atoms can be substituted with the same or different alkyl residues and/or aryl residues, which here are represented generally by the residues  $R_1$ - $R_4$  (this to say that the number of the different residues is not necessarily limited to 4).  $n$  can take on values from  $3/2$  to 20. Fractional numbers for  $n$  take into account that uneven numbers of siloxy groups can be present in the ring.

Phenyltrimethicone is advantageously selected as silicone oil. Other silicone oils can also be used advantageously within the scope of this invention, for example dimethicone, phenyldimethicone, cyclomethicone (octamethylcyclotetrasiloxane), for example hexamethylcyclotrisiloxane, polydimethylsiloxane, poly(methylphenylsiloxane), cetyl dimethicone, behenoxydimethicone.

Mixtures of cyclomethicone and isotridecyl isononanoate and of cyclomethicone and 2-ethylhexyl isostearate are also advantageous.

However, it is also advantageous to select silicone oils of similar constitution to be compounds indicated above, whose organic side chains have been derivatized, for example polyethoxylated and/or polypropoxylated.

Among these are, for example, polysiloxane, polyalkyl polyether copolymers like cetyl dimethicone copolyol, (cetyl dimethicone copolyol (and) polyglyceryl 4-isostearate (and) hexyl laurate).

The cationic surfactants used in accordance with the invention can preferably be selected from the group of the quaternary ammonium compounds, provided these do not have film forming properties, especially benzyltrialkylammonium chlorides or bromides such as benzyl dimethylstearyl ammonium chloride, also alkyl trialkyl ammonium salts, for example cetyltrimethylammonium chloride or bromide, alkyldimethylhydroxyethylammonium chlorides or bromides, dialkyldimethylammonium chlorides or bromides, alkylamidoethyltrimethylammonium ether sulfates, alkylpyridinium salts, for example lauryl- or cetylpyrimidinium chloride, imidazoline derivatives and compounds with cationic character like



amine oxides, for example alkyl dimethylamine oxides or alkylaminoethyl dimethylamine oxide. In particular, cetyltrimethylammonium salts can be advantageously used.

It can also prove to be particularly advantageous in accordance with the invention if the silicone oils are derivatized in the form that they have one or more quaternary ammonium groups in one or more organic residues, for example diquaternary polydimethyl di[si]loxanes like quaternium 80 or dimethicone propylbetaine and the like.

Besides the cationic surfactants that are obligatory in accordance with the invention, preparations in accordance with the invention can also contain anionic, nonionic and/or amphoteric surfactants, for example traditional soaps, for example fatty acid salts of sodium, alkyl sulfates, alkyl ether sulfates, alkanes and alkylbenzene sulfonates, sulfoacetates, sulfobetaines, sarcosinates, amidosulfobetaines, sulfosuccinates, sulfosuccinic acid semiesters, alkyl ether carboxylates, protein fatty acid condensates, alkylbetaines and amidobetaines, fatty acid alkanol amides, polyglycol ether derivatives.

Preparations for hair care in accordance with the invention can also optionally be advantageously used for cleansing the hair and the scalp.

Cosmetic preparations that are cosmetic cleansing preparations for the hair or the scalp can be in liquid or semisolid form, for example as gels. The preparations contain at least one cationic surface-active substance and mixtures thereof. They can also, if desired, contain anionic, nonionic and/or amphoteric surface-active substances or mixtures thereof, optionally electrolytes and auxiliary agents, as are usually used for such preparation. The surface-active substance can preferably be present in the cleansing preparations in a concentration between 1 and 30 wt%, with respect to the total weight of the preparations.

Cosmetic preparations that are shampoos preferably additionally contain at least one ionic, nonionic or amphoteric surface-active substance or mixture thereof, optionally electrolytes and auxiliary agents, as are usually used. The surface-active substance can preferably be present in the cleansing agents in a concentration between 0.1 and 5 wt%, with respect to the total weight of the preparation.

The preparations in accordance with the invention that are intended for cleansing the hair or the scalp contain, besides the said surfactants, water and optionally the additives that are conventional in cosmetics, for example perfumes, thickeners, dyes, deodorants, antimicrobial agents, remoisturizing agents, complexing and sequestering agents, perlescence agents, plant extracts, vitamins, active agents, and the like.

In spite of their oil content, the preparations in accordance with the invention surprisingly have very good foam formation and high cleaning power and to a high degree have a regenerating effect with respect to the general condition of the skin. In particular, the

preparations in accordance with the invention have smoothing effect on the skin reduce the feeling of skin dryness and make the skin supple.

Such embodiment of the preparations in accordance with the invention provides care to hair damaged or stressed by environmental influences or guard against such environmental influences. Also, the preparations in accordance with the invention give the hairstyle a looser fullness and firmness without having a sticky effect. They serve to increase the hair fullness, to improve the hair body and the hair volume as well as the whole of the hairstyle.

The microemulsions in accordance with the invention are preferably produced by bringing a mixture of the basic components, including an aqueous phase, oil phase, one or more of the O/W emulsifiers in accordance with the invention, optionally one or more W/O emulsifiers, and optionally other auxiliary substances additives and/or active agents, which form an O/W emulsion under the phase inversion temperature range, to a temperature above or within the phase inversion temperature range, and then cooling the microemulsion that is formed to room temperature. This preferably takes place while stirring the mixture.

It is in each case possible to avoid a homogenization step.

A method for producing O/W microemulsions that includes the following is likewise seen as an advantageous embodiment of this invention:

- (1) an aqueous phase, optionally containing the conventional substances that are soluble or dispersible in water,
  - (2) an oil phase, which optionally contains the conventional substances that are soluble or dispersible in said oil phase,
  - (3) one or more polyethoxylated O/w emulsifiers and/or one or more polypropoxylated O/W emulsifiers and/or one or more polyethoxylated and polypropoxylated O/W emulsifiers,
  - (4) optionally one or more W/O emulsifiers
  - (5) at least one cationic surfactant, that does not have film forming properties,
- which is characterized by the fact that

- (a) the initial concentrations of the oil phase, aqueous phase and optionally one or more W/O emulsifiers are selected and these components are added together,
- (b) the initial concentration of the O/W emulsifier(s), which can optionally be equal to zero, is selected and said O/W emulsifier(s) is/are added to the mixture obtained in (a),
- (c) where the mixture obtained in (b) has a starting temperature
- (d) the mixture obtained in (b): by appropriate variation of at least one parameter selected from the temperature and the concentration(s) of at least one of the selected emulsifiers and/or the oil phase and/or the aqueous phase, the resulting mixture passes through the phase inversion range between W/O emulsions and O/W emulsions and is brought into the range where the mixture is in the form of an O/W emulsion or O/W microemulsion,

(e) the mixture obtained in (d) is then optionally subjected to additional processing steps.

Equally advantageous in accordance with the invention are methods in which the variation of the parameter(s) consists of

(d1) varying the temperature of the mixture for a given concentration of the O/W emulsifier or the plurality of O/W emulsifiers and the aqueous phase and oil phase, or

(d2) varying the concentration of at least one O/W emulsifier for a given temperature, or

(d3) varying the concentration of the oil phase or the concentration of the aqueous phase for a given temperature and a given concentration of at least O/W emulsifier.

It can optionally be preferably in accordance with the invention to vary several parameters at the same time or in succession.

In accordance with the invention, advantageous hair care preparations can be obtained when the amount of polyethoxylated or polypropoxylated or polyethoxylated and polypropoxylated emulsifiers is under 1.5 wt%, especially under 1.0 wt%, with respect to the total weight of the preparation and less than 0.5 wt% of one or more cationic surfactants is present.

Figure 1 shows a highly simplified representation of a phase diagram. The variable parameter P is plotted against the temperature  $\theta$  as the second variable. P in this case represents a concentration parameter, either the amount of the oil phase, the amount of the aqueous phase, or the concentration of an emulsifier or an emulsifier mixture. For systems in accordance with the invention an O/W emulsion is present at lower temperature and can pass through the phase inversion region as the temperature is increased. With a further increase of the temperature W/O emulsions are observed. The structure of the system in the phase inversion region to all appearances is not critical for this invention. For example, it is conceivable that in the phase inversion region there will be lamellar phases, bicontinuous phases, cubic, hexagonal or inversely hexagonal phases, and also that the phase inversion region is composed of several like or more or less different phases.

The phase inversion region can be mathematically represented as a point within the linear coordinate system  $\Sigma$ , which is formed by the parameters temperatures, the concentration of a suitable emulsifier or emulsifier mixture in the preparation and the relevant concentrations of the oil phase and the aqueous phase, according to:

$$\Sigma = \{O, \theta, m, H, W\}$$

where O is the coordinate origin

$\theta$  is temperature

m is the concentration of the emulsifier or emulsifier mixture

H is the concentration of the oil phase

W is the concentration of the aqueous phase.

Strictly speaking one must of course take into account the contribution of each individual emulsifier to the overall function in a multi-component emulsifier system, which in the case of an  $i$ -component emulsifier system leads to the equation

$$\Sigma = \{O, \theta, m_1, m_2, \dots, m_i, H, W\}.$$

The phase inversion region  $\Phi$  in the mathematical sense is a cohesive region or a plurality of cohesive regions within the coordinate system  $\Sigma$ .  $\Phi$  represents the total quantity of the coordinate points  $K(\theta, a, m_1, m_2, \dots, m_i, H, W)$ , which determine mixtures in accordance with the invention of an aqueous phase of concentration  $W$ , an oil phase of concentration  $H$ ,  $i$  emulsifiers in accordance with the invention of concentration  $m_i$  at temperature  $\theta$ , and for which phase inversion occurs in the transition from a coordinate  $K_1 \notin \Phi$  to a coordinate  $K_2 \in \Phi$ , as described in Figure 2.

It is unimportant here if the phase inversion region of a given system is a single cohesive  $(i + 3)$ -dimensional region or consists of several such cohesive, but separate regions, thus several phase inversion regions of a given system. Within the scope of the disclosure presented here we will for this reason generally always speak of "the one" or "a" phase inversion region, even if two or more separate regions of this kind are present.

In Figure 2 the variable coordinates are temperature  $\theta$  and the concentration parameters  $P$  that are listed above, where it can be left open which particular concentration parameters these are. In the transition from  $K_1$  to  $K_2$  only the temperature is increased, and the other variables are kept constant.

Under the conditions in accordance with the invention this process is not reversible, i.e., if the system returns from coordinate  $K_2 \in \Phi$  back to coordinate  $K_1 \notin \Phi$ , transparent O/W microemulsions in accordance with the invention can be preserved.

Accordingly, the practice of producing a microemulsion in accordance with the invention advantageously consists of, after choosing the appropriate raw materials, i.e., the aqueous and oil phase, one or more O/W emulsifiers used in accordance with the invention, the latter preferably in concentrations at which inversion is possible for the given mixture, and optionally additional substances, bringing the individual components together while stirring, causing phase inversion by increasing the temperature of the mixture, then allowing the mixture to cool to room temperature while continuing to stir it.

However, it is also possible to vary more than one parameter at the same time, as shown in Figure 3. In Figure 3 the concentration of the aqueous phase is plotted against temperature. starting from the coordinate  $K_1 \notin \Phi$  the coordinates  $K_2 \notin \Phi$ , and  $K_4 \notin \Phi$ , or  $K_3 \in \Phi$ , can be achieved by increasing the temperature, while maintaining all of the other parameters. Starting from coordinates  $K_3$  and  $K_4$  it is possible to obtain O/W microemulsions in accordance with the invention by lowering the temperature back to  $K_1$  while maintaining all of the other parameters.

Starting from coordinates  $K_3$  and  $K_4$  it is possible to reach the coordinate  $K_5$  and obtain O/w microemulsions in accordance with the invention by lowering the temperature and by additional variation of the concentration of the oil phase, through the addition of water in Figure 3.

In view of Figure 3, it is consistent that, starting from coordinate  $K_4$ , although this coordinate is outside of the phase inversion region, that systems can be obtained similar to those that start from  $K_3$ , since even starting from  $K_4$  the phase inversion region must necessarily be crossed if the temperature is lowered.

Coordinate  $K_5$  can also be reached from coordinate  $K_1$  by varying the concentration of the aqueous phase, for example by adding water, as shown in Figure 3, and O/W microemulsions in accordance with the invention can be obtained. In this regard it must however be mentioned at the outset that in this case an O/W microemulsion in accordance with the invention, as it were as a concentrate, must already be present and it is then converted to an O/W microemulsion of altered composition in accordance with the invention by dilution.

However, considering everything it was astonishing and thus made available via independent inventive activity that starting from coordinate  $K_2$  lying outside the phase inversion region, be it by simple variation of the temperature back to coordinate  $K_1$  or additional variation of the concentration of the oil phase, for example by additional dilution with an aqueous phase to coordinate  $K_5$ , O/W emulsions in accordance with the invention can be obtained without passing through phase inversion. This appears to be advantageous in that a mixture of the basic components including water, oil phase, one or more O/W emulsifiers used in accordance with the invention, optionally one or more W/O emulsifiers, and optionally other auxiliary agents, additives and/or active agents, which form an O/W emulsion under the phase inversion temperature region, is brought to a temperature

- at which the components soluble in the oil phase are present either in dissolved or at least molten state
  - and which corresponds at least to the melting point of the highest melting oil component not present in a dissolved state,
  - which lies under the phase inversion temperature region of the system,
- and the O/W emulsion is then cooled to room temperature while forming an O/W microemulsion. This preferably takes place with stirring.

This method in accordance with the invention is particularly suitable when heat-sensitive or highly volatile substances are to be added to the O/W microemulsions in accordance with the invention. Moreover, this method, which is to be conducted at relatively low temperatures, is an energy-sparing method when compared to other methods.

Figure 4 describes the case in which at coordinate  $L_1$  there is initially no O/W emulsifier in accordance with the invention and in which the system is brought to a coordinate  $L_3 \notin \Phi$  or to a coordinate  $L_2 \notin \Phi$ , by increasing the temperature. Of course,  $L_2$  can also be reached by cooling a system that is at coordinate  $L_3$ .  $L_2$  and  $L_3$ , in which W/O emulsions, for example, can be present, differ in principle only by the fact that the temperature assigned to  $L_3$  is higher than any temperature that can be assigned to the phase inversion temperature region.

The presence of an additional W/O emulsifier for systems that are symbolized in Figure 4 is not unconditionally necessary, advantageous. The addition of an O/W emulsifier or several such emulsifiers in accordance with the invention at coordinates  $L_2$  or  $L_3$ , while lowering the temperature, moves the system to  $L_4$ , at which an O/W microemulsion in accordance with the invention is then present.

Another advantageous embodiment of the method in accordance with the invention accordingly consists of, after choosing appropriate raw materials, i.e., water phase and oil phase and optionally additional substances, to bring the individual components while stirring to a temperature at which phase inversion is possible for the given mixture and causing phase inversion by adding the O/W emulsifier(s) used in accordance with the invention to the mixture, after which the mixture is allowed to cool to room temperature while continuing to stir it.

It does not go beyond the knowledge of the specialist to determine, by simple tests, the appropriate temperature range within which a given mixture can undergo phase inversion. Normally this temperature range should be chosen between 70 and 95°C, but in an individual case it can be situated higher or lower than that.

In practice it is possible and possibly even advantageous to exceed the temperature range that can be assigned to the phase inversion region in making a microemulsion in accordance with the invention, since in the cooling to room temperature this range will then necessarily have to be passed through.

The addition of electrolytes causes a change of the solubility behavior of a hydrophilic emulsifier. For this reason the microemulsions in accordance with the invention advantageously contain electrolytes, especially one or more salts with the following anions: chlorides, also inorganic oxo element anions, in particular sulfates, carbonates, phosphates, borates and aluminates. Also, electrolytes based on organic anions can be used with advantage, for example lactates, acetate, benzoates, propionates, tartrates, citrates and others. Comparable effects can also be achieved by ethylenediaminetetraacetic acid and its salts.

Preferably ammonium, alkylammonium, alkali metal, alkaline earth metal, magnesium, iron or zinc ions are used as cations for the salts. It does not need to be mentioned that in cosmetics only physiologically harmless electrolytes should be used. Particular medical applications for the microemulsions in accordance with the invention can on the other hand, at

least in principle, condition the use of electrolytes that should not be used without medical supervision.

Potassium chloride, sodium chloride, magnesium sulfate, zinc sulfate and mixtures of these are especially preferred. Salt mixtures as occur in the natural salt from the Dead Sea are likewise advantageous.

The concentration of the electrolyte(s) should be about 0.1-10.0 wt%, especially advantageously about 0.3-8.0 wt%, with respect to the total weight of the preparation.

The preparations in accordance with the invention can be in the form of aerosols, thus preparations that are sprayable from aerosol containers, squeeze bottles or via a pumping device, or in the form of liquid compositions that can be applied by means of roll-on devices, as well as microemulsions that can be applied from ordinary bottles and containers.

The conventional known volatile liquefied propellants are suitable as propellants for the cosmetic deodorants in accordance with the invention that can be sprayed from aerosol containers, for example hydrocarbons (propane, butane, isobutane), and these can be used by themselves or in a mixture with each other. Pressurized air is also advantageously used.

Of course, the specialist is aware that there are substantially nontoxic propellant gases that would in principle be suitable for this invention, but which nevertheless must be rejected because of their harmful effect on the environment or other attendant circumstances, especially fluorochlorocarbons ("FCKW").

Moreover, it surprisingly turned out that when using the propellants that are soluble in the oil phase, for example the usual propane-butane mixtures, the O/W microemulsions in accordance with the invention are sprayed not simply as aerosol droplets but rather developed into fine-bubbled rich foams as soon as systems charged with such propellants experience a release of pressure.

Such post-foaming preparations are for this reason likewise to be seen as advantageous embodiments of this invention with independent inventive activity.

When using propellants that are insoluble in the oil phase the O/W microemulsions are sprayed as aerosol droplets.

In accordance with the invention, the preparations advantageously contain one or more antioxidants. All of the oxidants that are conventional or suitable for cosmetic and/or dermatologic applications can be used as favorable, but nevertheless the optionally used, antioxidants. Here it is advantageous to use oxidants as individual classes of active agents, for instance when a cosmetic or dermatologic application is of immediate priority, as in combating oxidative stress on the skin. However, it is also favorable to provide the microemulsions in accordance with the invention with a content of one or more antioxidants when the preparations are intended to serve another purpose, for example as deodorants or sunscreens.

The antioxidants are especially advantageously selected from the group consisting of amino acids (for example histidine, tyrosine, tryptophan) and their derivatives, imidazoles (for example urocanic acid) and their derivatives, peptides like D,L-carnosine, D-carnosine, L-carnosine, and their derivatives (for example anserine), carotenoids, carotenes (for example  $\alpha$ -carotene,  $\beta$ -carotene, lycopene) and their derivatives, lipoic acid and its derivatives (for example dihydrolipoic acid), aurothioglucose, propylthiouracil and other thiols (for example thioredoxin, glutathione, cysteine, cystine, cystamine and their glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl,  $\gamma$ -linoleyl, cholesteryl and glyceryl esters) and their salts, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and its derivatives (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulfoximine compounds (for example buthioninesulfoximine, homocysteinesulfoximine, buthioninesulfones, penta-, hexa-, heptathioninesulfoximines) in very low compatible dosages (for example pmol to  $\mu\text{mol/kg}$ ), also (metal) chelators (for example,  $\alpha$ -hydroxy fatty acids,  $\alpha$ -hydroxypalmitic acid, phytic acid, lactoferrin),  $\alpha$ -hydroxy acids (for example citric acid, lactic acid, malic acid), humic acid, gallic acid, chlorogenic acid, caffeic acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and their derivatives, unsaturated fatty acids and their derivatives (for example  $\gamma$ -linolenic acid, linoleic acid, oleic acid), folic acid and its derivatives, ubiquinone and ubiquinol [and] their derivatives, vitamin C and derivatives (for example ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (for example vitamin E acetate), vitamin A and derivatives (vitamin A palmitate) and coniferyl benzoate of benzoic resin, rutic acid and its derivatives, ferulic acid and its derivatives, butylhydroxytoluene, butylhydroxyanisole, nordihydroguaiaric acid, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and its derivatives, zinc and its derivatives (for example ZnO, ZnSO<sub>4</sub>), selenium and its derivatives (for example selenium methionine), stilbene and its derivatives (for example stilbene oxide, trans-stilbene oxide) and the derivatives of these active agents that are suitable in accordance with the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids).

The amount of the antioxidants (one or more compounds) in the preparations is preferably 0.001 to 30 wt%, especially preferably 0.05-20 wt%, especially 1-10 wt%, with respect to the total weight of the preparation.

Of course, it is known to the specialist that upmarket cosmetic preparations are for the most part not conceivable without the usual auxiliary aids and additives. Among these are, for example, bodying agents, fillers, fragrances, dyes, emulsifiers, additional active agents like vitamins or proteins, sunscreens, stabilizers, insect repellants, alcohol, water, water, salts, antimicrobial, proteolytic or keratolytic substances, etc.

If desired, the aqueous phase of the O/W microemulsions in accordance with the invention can also contain thickeners, so that the overall preparation appears to be gel-like and is



to be interpreted as a microemulsion gel. Carrageen or PEG-4 rapeseed amides as well as laureth-2 amide MEA, for example, has proven to be suitable thickeners.

In accordance with the invention active agents can also be chosen with great advantage from the group of lipophilic active agents, especially from the following group:

acetylsalicylic acid, atropine, azulene, hydrocortisone, and its derivatives, for example, hydrocortisone 17-valerate, vitamins, for example ascorbic acid and its derivatives, vitamins of the B and D series, especially vitamin B<sub>1</sub>, vitamin B<sub>12</sub>, vitamin D<sub>1</sub>, and also bisabolol, unsaturated fatty acids, namely the essential fatty acids (often called vitamin F), especially gamma-linolenic acid, oleic acid, eicosapentaenoic acid, docosahexaenoic acid and its derivatives, chloramphenicol, caffeine, prostaglandins, thymol, camphor, extracts or other products of plant and animal origin, for example primrose oil, borage oil, carob seed oil, fish oil, cod liver oil, or also ceramides and ceramide-like compounds, and so forth.

Although, of course, the use of hydrophilic active agents is favored in accordance with the invention, another advantage of the microemulsions in accordance with the invention is that the high amount of finely divided droplets specifically makes the oil soluble, or lipophilic, active agents biologically available with particularly high efficacy.

It is also advantageous to choose the active agents from among remoisturizing substances, for example purcellin oil, Eucent® and Neocent®.

The preparations in accordance with the invention can contain cosmetic auxiliary agents, as are usually used in such preparations, for example preservatives, bactericides, virucides, fragrances, substances to prevent foaming, dyes, pigments that have colorant action, thickeners, surface-active substances, emulsifiers, softening, moisturizing and/or moisture-holding substances, anti-inflammatory substances, medications, fats, oil, waxes or other normal components of a cosmetic or dermatologic formulation like alcohols, polyols, polymers, foam stabilizers, electrolytes, organic solvents.

Mixtures of the said solvents are used with particular advantage.

Other substances that can be used as components include fats, waxes and other natural and synthetic fat bodies, preferably esters of fatty acids with low carbon number alcohols, for example isopropanol, propylene glycol or glycerol, or esters of fatty alcohols with alkanoic acids that have a low number of carbon atoms or with fatty acids, alcohols, diols or polyols with low numbers of carbon atoms, as well as their ethers, preferably ethanol, isopropanol, propylene glycol, glycerol, ethylene glycol, ethylene glycol monoethyl or monobutyl ethers, propylene glycol monomethyl, monoethyl or monobutyl ethers, diethylene glycol monomethyl or monoethyl ethers and similar products.

The following examples are intended to illustrate this invention.

Example 1

	wt%
Isoceteth-20	0.80
Glyceryl isostearate	0.40
Phenyl trimethicone	0.50
Cetrimonium chloride	0.34
Fragrance and preservatives	q.s.
Water, to	100.00

Example 2

	wt%
Glyceryl isostearate	0.33
Isoceteth-15	0.93
Octyl isostearate	0.60
Cyclomethicone	1.20
Cetrimonium chloride	0.40
Fragrance and preservatives	q.s.
Water, to	100.00

Example 3

	wt%
Sorbitan monoisostearate	0.42
Isoceteth-15	0.84
Isotridecyl isononanoate	0.60
Cyclomethicone	1.20
Cetrimonium chloride	0.40
Fragrance and preservatives	q.s.
Water, to	100.00

Example 4

	wt%
Diglyceryl monoisostearate	0.42
Isoceteth-15	0.84
Isotridecyl isononanoate	0.50
Cyclomethicone	1.20
Cetrimonium chloride	0.40

Fragrance and preservatives	q.s.
Water, to	100.00

Example 5

	wt%
Glyceryl isostearate	0.44
PEG-60 evening primrose glyceride	0.87
Isotridecyl isononanoate	0.60
Cyclomethicone	1.20
Cetrimonium chloride	0.45
Propylene glycol	0.55
Fragrance and preservatives	q.s.
Water, to	100.00

Example 6

	wt%
Glyceryl isolaurate	0.83
Laureth-11 carboxylic acid (90%)	0.68
Cetearyl isononanoate	0.32
Cyclomethicone	0.53
Cetrimonium chloride	0.40
Fragrance and preservatives	q.s.
Water, to	100.00

Example 7

	wt%
Glyceryl isostearate	0.44
PEG-20 stearate	0.87
Isotridecyl isononanoate	0.50
Cyclomethicone	0.61
Cetrimonium chloride	0.38
Fragrance and preservatives	q.s.
Water, to	100.00

Example 8

	wt%
Glyceryl isostearate	0.44
Ceteareth-15	0.87
Caprylic/capric triglycerides	0.60
Cyclomethicone	0.80
Cetrimonium chloride	0.40
Fragrance and preservatives	q.s.
Water, to	100.00

Example 9

	wt%
Glyceryl isostearate	0.34
Ceteareth-15	0.77
Dicapryl ether	0.80
Cetrimonium chloride	0.40
Fragrance and preservatives	q.s.
Water, to	100.00

Example 10

	wt%
Diglyceryl monoisostearate	0.28
Ceteareth-15	0.76
Liquid paraffin	0.70
Cetrimonium chloride	0.35
Fragrance and preservatives	q.s.
Water, to	100.00

Example 11

	wt%
Diglyceryl monoisostearate	0.28
Ceteareth-15	0.82
Octyldodecanol	0.80
Cetrimonium chloride	0.35
Fragrance and preservatives	q.s.
Water, to	100.00

Example 12

	wt%
PEG-6 caprylic/capric acid glycerides	0.87
Isotridecyl isononanoate	0.30
Cyclomethicone	0.61
Cetrimonium chloride	0.35
Fragrance and preservatives	q.s.
Water, to	100.00

Example 13

	wt%
Glyceryl isostearate	0.44
Isotridecyl isononanoate	0.30
PEG-20 glyceryl isostearate	0.87
Cyclomethicone	0.60
Cetrimonium chloride	0.40
Fragrance and preservatives	q.s.
Water, to	100.00

Claims

1. Hair care preparations in form of a transparent or translucent microemulsion of oil-in-water type,

- including an oil phase, and an aqueous phase

- containing:

one or more polyethoxylated O/W emulsifiers and/or

one or more polypropoxylated O/W emulsifiers and/or

one or more polyethoxylated and polypropoxylated O/W emulsifiers,

- optionally also containing one or more W/O emulsifiers

- also containing at least one cationic surfactant selected from among the surfactants that do have film-forming properties

- an emulsifier content less than 2.0 wt% with respect to the total weight of the emulsion.

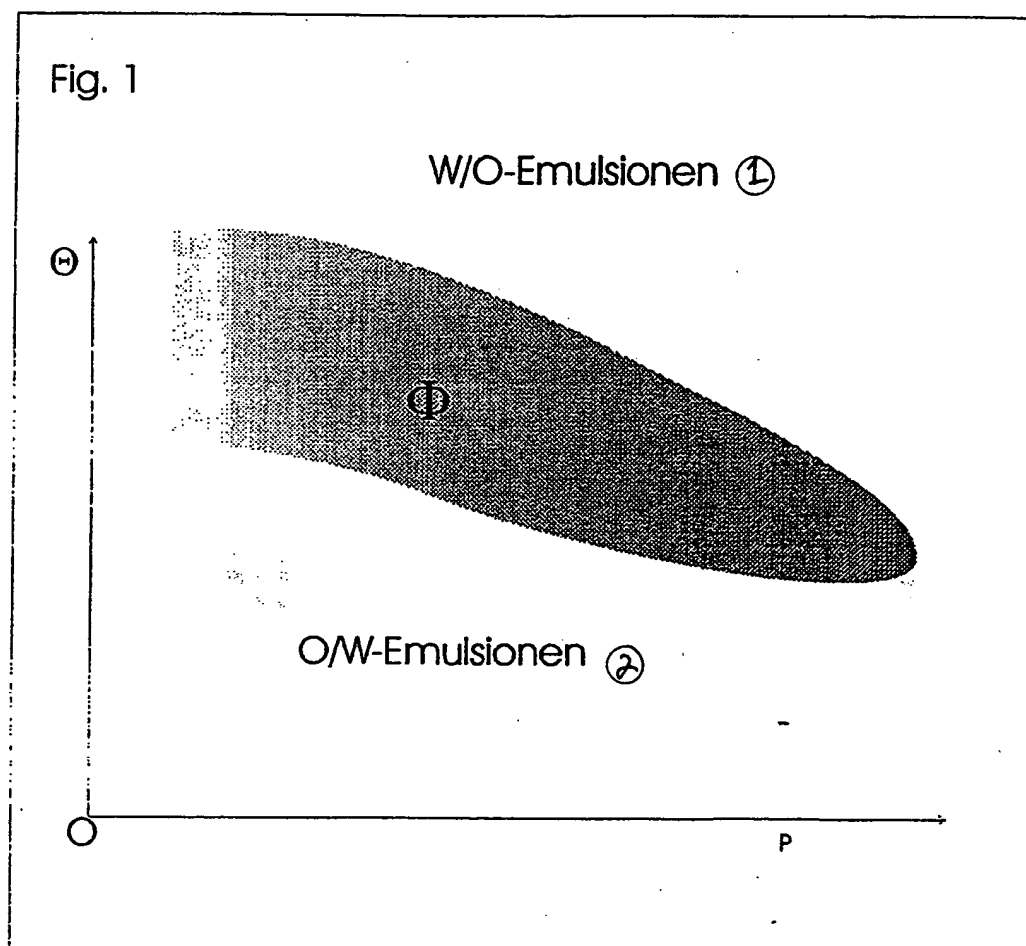
2. The use of preparations as in Claim 1 to increase the fullness of hair, to improve the hair body and the hair volume as well as the hold of the hairstyle.

3. Preparations as in Claim 1 or a use as in Claim 2, which are characterized by the fact that the oil phase is chosen from among silicone oils, especially from among phenyltrimethicone, cyclomethicone (octamethylcyclotetrasiloxane), hexamethylcyclotrisiloxane,

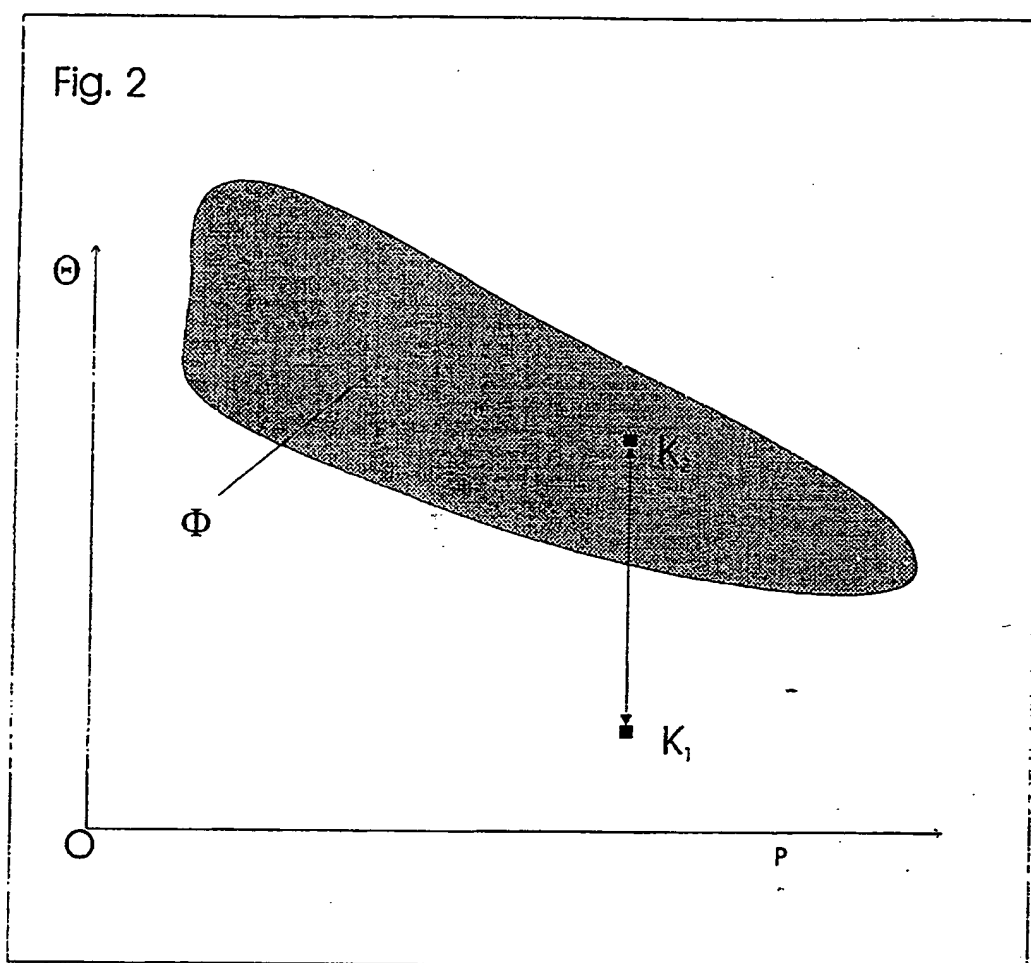
polydimethylsiloxane, poly(methylphenylsiloxane), as from cyclomethicone and isotridecyl isononanoate, and mixtures of cyclomethicone and 2-ethylhexyl isostearate.

4. Preparations as in Claim 1 or a use as in Claim 2, which are characterized by the fact that the cationic surfactant(s) is/are chosen from among the quaternary ammonium compounds, provided these do not have film forming properties, especially benzyldialkylammonium chlorides or bromides such as benzyldimethylstearylammmonium chloride, also alkylalkylammmonium salts, for example cetyltrimethylammmonium chloride or bromide, alkylmethylhydroxyethylammmonium chlorides or bromides, dialkylmethylammmonium chlorides or bromides, alkylamidoethyltrimethylammmonium ether sulfates, alkylpyridinium salts, for example lauryl- or cetylpyrimidium chloride, imidazoline derivatives and compounds with cationic character like amine oxides, for example alkylmethylamine oxide or alkylaminoethylmethylamine oxides.

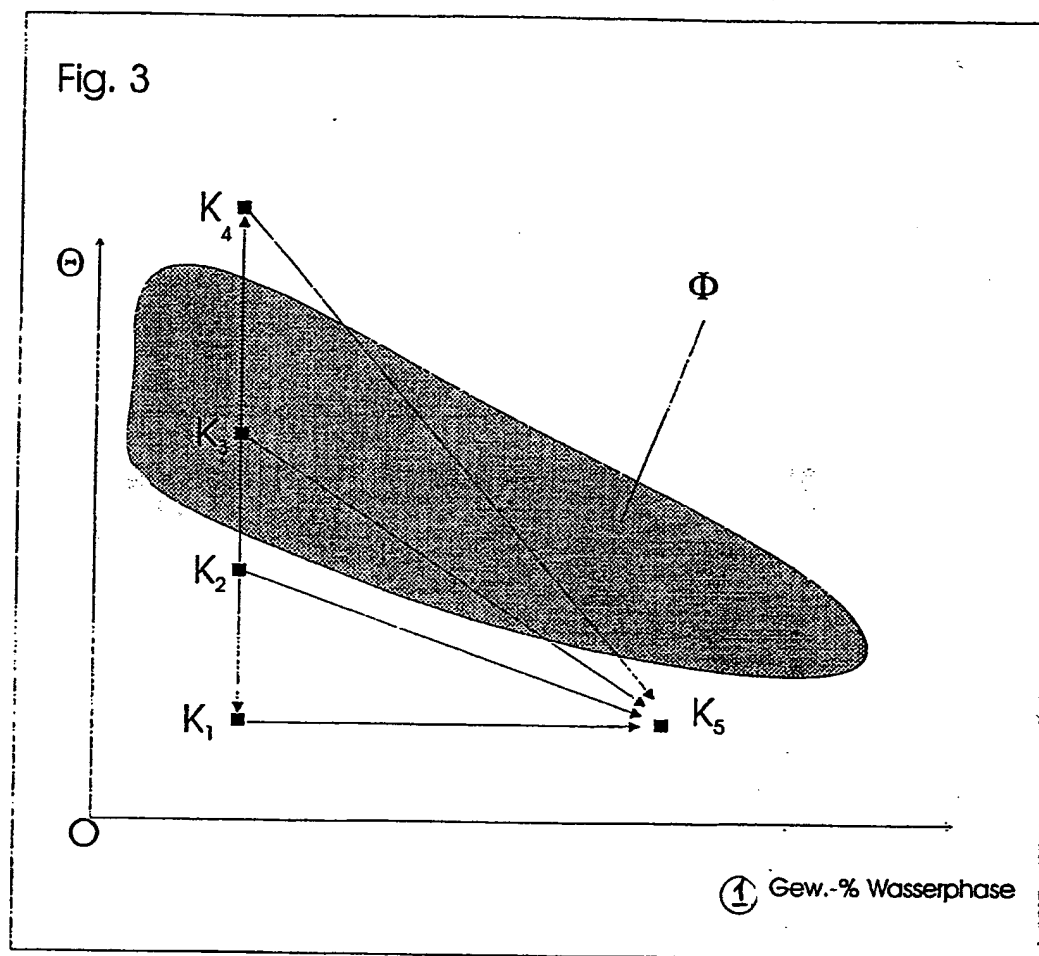
With 4 page(s) of drawings



Key: 1 W/O emulsions  
2 O/W emulsions







Key: 1. wt% aqueous phase

